PART ONE
NUCLEAR ALKYLATION AND REPLACEMENT REACTIONS INVOLVING HINDERED KETONES

PART TWO
THE REARRANGEMENT OF *ALPHA*-HALOKETONES IN THE PRESENCE OF BASE

BY

ROGER JAMES TULL

B.S., Michigan State College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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PART ONE

NUCLEAR ALKYLATION AND REPLACEMENT REACTIONS INVOLVING HINDERED KETONES

Introduction

It has been found that if one of the phenyl groups in benzophenone is replaced by a duryl radical, the carbonyl group is hindered to a point that its function in reactions with Grignard reagents is almost entirely restricted to its directive influence in the unsubstituted benzene ring. For example, benzoyldurene can be alkylated in the *para* position of the unsubstituted benzene ring by the action of *t*-butyl- and benzylmagnesium chloride (1). The replacement of methoxyl groups *ortho* to hindered carbonyl groups by the Grignard reagent is a well-established reaction (2).

In the present work, a study was made of the behavior of benzoyldurene and its derivatives toward the Grignard reagent.

Discussion Of Results

Isopropylmagnesium bromide and cyclohexylmagnesium chloride were found to be effective alkylating agents. These reagents converted benzoyldurene into *p*-isopropylbenzoyldurene and *p*-cyclohexylbenzoyldurene, respectively. The most effective reagent was *s*-butylmagnesium bromide which afforded a 63% yield of *p*-*s*-butylbenzoyldurene. The structures of the *para* alkylation products were established by independent syntheses involving well-known procedures.

Since the *para* position in the duryl ring was unaffected in these reactions, it was predicted that the introduction of electron-donating methyl groups into the phenyl ring of benzoyldurene would tend to render alkylation more difficult. Accordingly, *o*-toluyldurene and 2,6-dimethylbenzoyldurene

were treated with *t*-butylmagnesium chloride. In each case the alkyl radical entered the *para* position of the less substituted ring, and the yields were very low. The 2,6-dimethylbenzoyldurene was prepared by the simultaneous replacement of both methoxyl groups in 2,6-dimethoxybenzoyldurene by the methyl Grignard reagent, the dimethoxy ketone being made by condensing the lithium derivative of resorcinol dimethyl ether with duroyl chloride. The structure of 4-*t*-butyl-2-methylbenzoyldurene was established by synthesis of the compound by treatment of *p*-*t*-butylbenzoyldurene with methylmagnesium iodide. A dihydro derivative was obtained which was aromatized by the use of palladium. The structure of 4-*t*-butyl-2,6-dimethylbenzoyldurene was proved by an independent synthesis involving the condensation of duroyl chloride with 4-*t*-butyl-2,6-dimethylphenylmagnesium bromide.

A new type of group replacement was discovered when *p*-cyanobenzoyldurene was allowed to react with methyl and benzyl Grignard reagents. The products were *p*-toluyldurene and *p*-benzylbenzoyldurene, respectively.

The four methoxyl groups in 2,2′,6,6′-tetramethoxybenzophenone were found to have little blocking effect on the carbonyl group. When this ketone was treated with methylmagnesium iodide only the corresponding ethylene was obtained, the product being formed as a result of normal 1,2 addition.

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PART TWO

THE REARRANGEMENT OF *ALPHA*-HALOKETONES IN THE PRESENCE OF BASE

Introduction

During the past few years considerable attention has been given to the rearrangement that occurs when ketones containing an α-halogen atom are treated with basic reagents. A typical example of this phenomenon is found in the conversion of 2-chlorocyclohexanone into cyclopentane carboxylic acid by the action of alkali (1). In 1939, Tchoubar and Sackur (2) suggested that the rearrangement probably involves the formation of an unstable cyclopropanone intermediate which is then cleaved to form the product. Recent experimental work has made this mechanism appear more promising, but no attempt has been made to test this theory by a critical examination of the results reported in the literature.

Accordingly, the purpose of this study was to present a survey of the accomplishments in this field, and to correlate, wherever possible, the results of these investigations with a mechanism involving the formation of a three-membered ring.

Discussion

In a majority of cases, the course of the rearrangement of α-haloketones can be explained by the assumption that the cyclopropanone ring is an essential intermediate. A typical piece of evidence for the existence of such an intermediate was obtained from the fact that chloromethyl benzyl ketone and its isomer α-chlorobenzyl methyl ketone form the same product, methyl dihydrocinnamate, in the presence of sodium methoxide (3). If an intramolecular alkylation took place, both isomers would be converted into the common intermediate, 2-phenylcyclopropanone. A cleavage of the latter by the methoxide ion would then produce methyl dihydrocinnamate.

Richard (4) has reported that desyl chloride rearranges

to yield diphenylacetic acid. Since desyl chloride is incapable of forming a three-membered ring, this rearrangement would appear to serve as conflicting evidence for the mechanism in question. However, the reaction was repeated and benzilic acid was the only alkali soluble product isolated. The formation of benzilic acid can be explained on the basis of an entirely different mechanism.

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VITA

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